confirmed by product studies (see Experimental Section). That is, the expected olefin, $B(H)C=CMe_2$, was not detected when B_2CH_2 was reacted with thermally generated $BO\cdot$ or when B_2CHCl was reacted with sodium. The absence of olefin provides some support for the slow first-order decay occurring by an intermolecular 1,3 hydrogen transfer. However, as was pointed out (see Experimental Section) the absence of olefin under conditions where the radicals are being generated continuously does *not* rule out its formation during the slow decay of "residual" $B_2\dot{C}H$ (and other radicals) that is epr monitored. Until $B_2\dot{C}H$ radicals can be "cleanly" generated in unreactive media and their products analyzed, the question as to their mode of slow decay must remain unanswered.

The preexponential factors for the first-order decay of several of the $B_2\dot{C}CH_2R$ radicals are impossibly low for true unimolecular reactions. We believe this is due to the incursion of second-order decay processes. That is, at sufficiently low temperatures the $B_2\dot{C}CH_2R$ radicals decay by a bimolecular reaction that is presumed to be a disproportionation. Some contribution from this process increases the apparent value of k^1_{epr} to an increasing extent as the temperature is lowered and as a consequence the Arrhenius plots are probably curves rather than straight lines and hence the apparent value of A^1_{epr} is reduced.

The first-order decay rates for $B_2\dot{C}CH_2R$ radicals increase along the series $R = C_6H_5 \ll OCF_3 \le CCl_3 < P(O)(OEt)_2 < Si\text{-}n\text{-}Bu_3 \ll SCF_3$. The reversible addition of thiyl radicals to olefins has been firmly established in many studies,[32] which suggests that the rapid decay of $B_2\dot{C}CH_2SCF_3$ is due to the facile elimination of $CF_3S\cdot$

$$B_2\dot{C}CH_2SCF_3 \longrightarrow B_2C=CH_2 + CF_3S\cdot$$
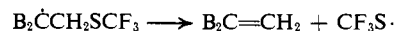
An analogous β scission may be responsible for the first-order decay of most of the other $B_2\dot{C}CH_2R$ radicals. However, we would not expect the C_6H_5 radical to be eliminated, and in keeping with this the $B_2\dot{C}CH_2C_6H_5$ radical is remarkably stable. It probably decays in a manner analogous to $B_2\dot{C}H$, $B_3\dot{C}$, etc., but it is not clear why it should be more stable than these radicals.

The rapid bimolecular decay of $(Me_3Si)_2\dot{C}H$ and of $B_2\dot{C}Cl$ appears to be anomalous, although it is likely that the former radical is not particularly hindered.[33] The peculiar behavior of $B_2\dot{C}Cl$ is perhaps a consequence of the strong dipole present in this radical, which by dipole–dipole interaction holds pairs of radicals in close proximity to one another for sufficient time for them to react.

(32) For leading references, see C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957; W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.

(33) For example, $(Me_3Si)_4C$ can be prepared readily,[34] but B_4C has yet to be prepared.

(34) See, e.g., H. Gilman and C. L. Smith, *J. Amer. Chem. Soc.*, **86**, 1454 (1964); R. L. Merker and M. J. Scott, *J. Organometal. Chem.*, **4**, 98 (1965); G. Kobrich and R. v. Nagel, *Tetrahedron Lett.*, 4693 (1970).

An Electron Spin Resonance Investigation of the 1-Aziridylcarbinyl and Related Free Radicals[1]

Wayne C. Danen* and Charles T. West

Contribution from the Department of Chemistry, Kansas State University, Manhattan, Kansas 66506. Received November 19, 1973

Abstract: The 1-aziridylcarbinyl radical (2) could conceivably prefer a bisected conformation (2a) in which radical stabilization is derived by interaction with the three-membered ring as in the cyclopropylcarbinyl radical or a perpendicular alignment (2b) in which interaction with the nitrogen lone pair is maximized. The 1-aziridylcarbinyl radical has been generated from *N*-methylaziridine by abstraction of hydrogen by photochemically generated *tert*-butoxyl radicals at $-136°$. The observed hyperfine couplings, $a^N = 10.68$ G and $a_\alpha{}^H = 17.07$ G, are consistent with a perpendicular conformation (2b) in contrast to the cyclopropylcarbinyl radical. INDO calculations support this conclusion predicting 2b to be more stable than 2a. At higher temperatures 2 undergoes ring opening to produce 4 in a manner analogous to the cyclopropylcarbinyl radical. Attempts to produce the (1-aziridyl)-1-ethyl radical (7) always gave spectra of the corresponding ring-opened radical 8. An out-of-phase line-width effect in the β-proton splittings was noted for 4 and 8 indicating a significant difference in conformation between these radicals and the related allylcarbinyl radical. It is suggested that a 1,3 interaction between the unpaired electron and the lone pair of electrons on the nitrogen atom may be preferred over interaction with the double bond. Efforts to produce the cyclopropylamino radical (3) yielded the ring-opened radical 11 in solution and the imino species 12 in an adamantane matrix. INDO calculations suggest that the bisected conformation 3a is more stable than the perpendicular alignment 3b.

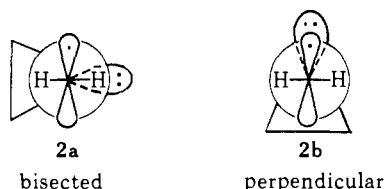Cyclopropylcarbinyl radicals have been the subject of investigation for a number of years in order to determine whether these radicals are nonclassical in nature in analogy to the purported nonclassical cyclopropylcarbinyl cation. Product analyses in systems generating cyclopropylcarbinyl and allylcarbinyl radicals indicated that both exist as classical radicals with the cyclopropylcarbinyl radical as an unstable inter-

mediate in allylcarbinyl rearrangements.[2,3] These conclusions have been supported by electron spin resonance (esr) studies[3] which, in addition, have indicated that the cyclopropylcarbinyl radical prefers the bisected conformation (1a) in preference to the perpendicular align-

1a
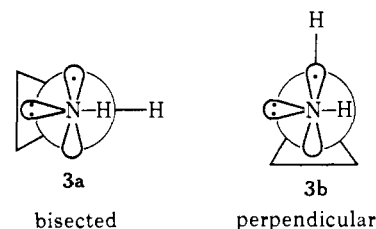bisected

1b
perpendicular
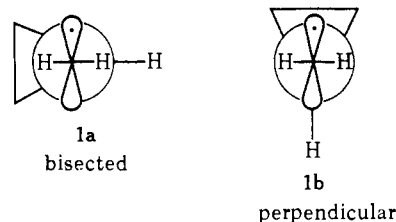
ment (1b) at least at $-140°$. Theoretical studies concur with the bisected conformation being lower in energy than the perpendicular conformation.[4] Warming the solution containing the cyclopropylcarbinyl radical to temperatures above $-140°$ produced the esr spectrum of the allylcarbinyl radical; there was no esr evidence for the formation of the cyclobutyl radical or the conversion of the allylcarbinyl radical to the cyclopropylcarbinyl radical.

As part of our continuing studies of nitrogen-containing free radicals,[1a,5] we believed it would be of interest to investigate other three-membered ring systems appropriately substituted with a nitrogen atom. The 1-aziridylcarbinyl system was chosen in view of the fact that the aziridine ring could conceivably stabilize the radical center from either the bisected or perpendicular conformations. Structure **2a** depicts the bi-

2a
bisected

2b
perpendicular

sected conformation in which radical stabilization is derived from the three-membered ring as in the cyclopropylcarbinyl radical and structure **2b** depicts the perpendicular conformation in which radical stabilization is derived from interaction with the nitrogen lone pair.

The cyclopropylamino radical is a second interesting system in that an unpaired electron and an electron pair reside on nitrogen simultaneously. Again, either bisected (**3a**) or perpendicular (**3b**) alignment of the cyclopropyl group is plausible. By analogy to INDO calculations on the cyclopropylcarbinyl cation, radical, and anion,[4] it would appear that the cyclopropylamino radical would prefer the bisected confor-
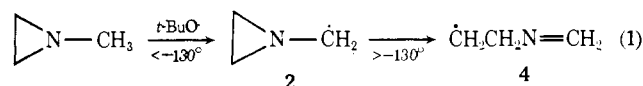

3a
bisected

3b
perpendicular

mation since calculations have shown that the cyclopropylcarbinyl anion prefers the perpendicular alignment. If the lone pair of electrons on nitrogen in the cyclopropylamino radical can be considered "carbanionlike," then the bisected conformation **3a** should be preferred because in such an alignment both the lone pair and the unpaired electron orbitals are simultaneously disposed to interact most favorably with the three-membered ring.

We presently wish to report that we have observed the 1-aziridylcarbinyl radical by esr and conclude that it exists in the perpendicular conformation **2b** in contrast to the cyclopropylcarbinyl radical which prefers the bisected alignment **1a**. The 1-aziridylcarbinyl radical undergoes a facile rearrangement analogous to the cyclopropylcarbinyl species. We were unsuccessful in observing a spectrum of the cyclopropylamino radical directly but did detect rearrangement products indicative of a cyclopropylamino radical precursor.
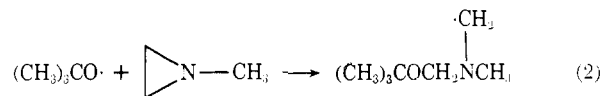
Results and Discussion

(a) 1-Aziridylcarbinyl Radical. The 1-aziridylcarbinyl radical was generated by hydrogen abstraction from N-methylaziridine in a manner analogous to that used for generating the cyclopropylcarbinyl radical.[3] Photolysis of a degassed solution containing 10% by volume N-methylaziridine and 10–30% by volume di-tert-butyl peroxide in cyclopropane at -140 to $-130°$ produced an esr spectrum consistent with the 1-aziridylcarbinyl radical **2** (Figure 1). At temperatures above

$$\text{N—CH}_3 \xrightarrow[\leftarrow -130°]{t\text{-BuO}\cdot} \text{N—}\dot{\text{C}}\text{H}_2 \xrightarrow{>-130°} \dot{\text{C}}\text{H}_2\text{CH}_2\text{N}=\text{CH}_2 \quad (1)$$

$$\quad\quad\quad 2 \quad\quad\quad\quad\quad\quad 4$$

$-130°$ an esr spectrum consistent with ring opening of the aziridylcarbinyl radical to produce **4** was obtained. No esr evidence for the azetidino radical[5e] was present. The esr spectral parameters of the aziridylcarbinyl and related radicals are provided in Table I.

The assignment of structure of radicals **2** and **4** was made on the following basis. The spectrum assigned to the 1-aziridylcarbinyl radical had only two observable hyperfine coupling constants (although the rather broad lines could conceivably obscure smaller splittings), a $1:2:1$ triplet due to two equivalent hydrogens and a $1:1:1$ triplet due to one nitrogen, thus ruling out a ring-opened structure from a homolytic ring cleavage (eq 2)

$$(\text{CH}_3)_3\text{CO}\cdot + \text{N—CH}_3 \longrightarrow (\text{CH}_3)_3\text{COCH}_2\overset{\cdot\text{CH}_2}{\underset{|}{\text{NCH}_3}} \quad (2)$$

since the $\gamma\text{-CH}_2$ and $\gamma\text{-CH}_3$ would be expected to have hfsc's on the order of 3.70 G as observed in the dimethylaminomethyl radical, $(\text{CH}_3)_2\text{N}\dot{\text{C}}\text{H}_2$.[6] Raising the temperature caused the esr spectrum to change to

(2) (a) C. Walling, "Molecular Rearrangements," Vol. I, P. deMayo, Ed., Interscience, New York, N. Y., 1963, p 440 ff; (b) L. K. Montgomery and J. W. Matt, J. Amer. Chem. Soc., **89**, 923, 934, 3050 (1967); (c) T. A. Halgren, M. E. Hawden, M. E. Medof, and J. D. Roberts, ibid., **89**, 3051 (1967).

(3) (a) J. K. Kochi, P. J. Krusic, and D. R. Eaton, J. Amer. Chem. Soc., **91**, 1877 (1969); see ref 1 and 2 of this article for additional references; (b) J. K. Kochi, P. J. Krusic, and D. R. Eaton, ibid., **91**, 1879 (1969).

(4) W. C. Danen, J. Amer. Chem. Soc., **94**, 4835 (1972), and references cited therein.

(5) (a) W. C. Danen and R. W. Gellert, J. Amer. Chem. Soc., **94**, 6853 (1972); (b) W. C. Danen and R. C. Rickard, ibid., **94**, 3254 (1972); (c) W. C. Danen and C. T. West, ibid., **93**, 5582 (1971); (d) W. C. Danen and T. T. Kensler, ibid., **92**, 5235 (1970); (e) Tetrahedron Lett., 2247 (1971).

(6) D. E. Wood and R. V. Lloyd, J. Chem. Phys., **53**, 3932 (1970).

Table I. Esr Spectral Parameters of Radicals from N-Alkylaziridines and Cyclopropylamine in Cyclopropane Solution[a]

Radical	a^N	a^H_α	a^H_β	a^H_γ	a^H_δ	$a^H_{CH_3}$	g[b]	Temp, °C	Ref
2	10.68	17.07					2.0027	−136	This work
4[c]	2.07	22.30	33.80		0.8 (1 H)			−100	This work
8[d]	1.67	21.90	34.40				2.0025	−110	This work
11[e]		22.35	28.80					−60	This work
12[f]	9.40		79.5 (1 H)	2.80 (2 H)			2.0030	R.T.	This work
$\dot{C}H_2CH_2CH=CH_2$ **(10)**		22.17	28.53	0.61 (1 H)	0.35 (1 H)			−90	3a
$\dot{C}H_2N(CH_3)_2$	7.03	13.35				3.70 (6 H)	2.0028	R.T.	6

[a] Hfsc's are reported in gauss and have estimated accuracies of ±0.5% except where noted. [b] Estimated accuracy ±0.0001. [c] Estimated accuracies of hfsc's ±1% due to weak signal. [d] Estimated accuracies of hfsc's ±2% due to calibration difficulties. [e] R = H or $(CH_3)_3CO$; see text. [f] In adamantane matrix.

a second carbon-centered radical **4**, which exhibited a large 1:2:1 triplet further split into a smaller 1:2:1 triplet, typical of a radical with the structure $\dot{C}H_2CH_2R$. The 1:1:1 nitrogen triplet of 2.07 G observed in the postulated ring-opened radical appeared reasonable for a γ nitrogen. Also, the doublet splitting of 0.8 G for **4** was particularly characteristic of an allylcarbinyl radical system with splitting by a single δ hydrogen.[3a]

The nitrogen hyperfine coupling of 10.68 G for the 1-aziridylcarbinyl radical **2** suggests that this radical exists in the perpendicular conformation **2b** on the time average at −136°. This contrasts the cyclopropylcarbinyl radical which prefers the bisected conformation **1a** at −140°.[3a] A significantly smaller a^N would result from the bisected alignment **2a** for the 1-aziridylcarbinyl radical. The magnitude of the nitrogen hfsc in **2a** can be estimated from the ^{13}C hfsc of 13.57 G of the β carbon in the ethyl radical[7] and the ratio of ^{14}N and ^{13}C magnetogyric ratios. The calculation, 13.57(1934/6728), yields a hyperfine coupling of 3.9 G. This hfsc is expected to arise from a spin polarization mechanism and therefore would be negative and independent of the conformation of the radical. This calculation is supported by the observation of a nitrogen coupling of 4.1 G in the $\dot{C}H_2NH_3{}^+$ radical in which the nitrogen interaction could arise only through a spin polarization mechanism.[8]

Additional evidence for a preferred perpendicular alignment of the 1-aziridylcarbinyl radical is available from a comparison of the 10.68 G nitrogen coupling observed for this radical with a variety of aliphatic aminoalkyl radicals, $RR'\dot{C}NR''R'''$, investigated by Wood and Lloyd.[6] These workers found that a^N varied from 3 to 7.3 G depending upon the degree of substitution of the trigonal carbon and the nitrogen. A nontwisted anti conformation was found for these aminoalkyl radicals and a substantial stabilization resulted from a three-electron π bond between the trigonal carbon and the nitrogen. The 10.68-G nitrogen coupling observed for **2** at −136° is greater than any of the aminoalkyl radicals reported at room temperature by Wood and Lloyd suggesting that **2** is likewise in a nontwist (i.e., perpendicular) alignment. The larger coupling observed for **2** could be the result of the different experimental temperatures influencing the possible configurations and/or conformational rotomers of such aminoalkyl radicals but we believe the larger a^N for **2** is more likely due to the high s character of the nitrogen lone pair in **2**. This increased s character

(7) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).
(8) R. P. Kohin and P. G. Nadeau, *J. Chem. Phys.*, **44**, 691 (1966).
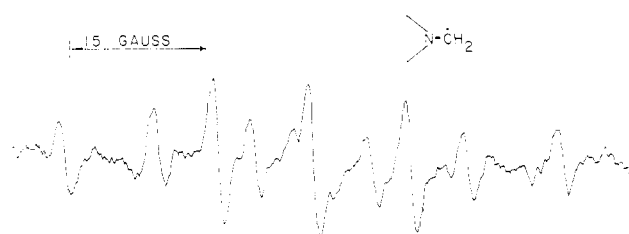
Figure 1. Electron spin resonance spectrum of the 1-aziridyl-carbinyl radical (**2**) at −136° formed by photolysis of N-methyl-aziridine and di-*tert*-butyl peroxide in cyclopropane solution.

relative to the open-chain aminoalkyl radicals results from the high p character of the C–N bonds in the strained three-membered aziridine ring and would cause a larger nitrogen interaction provided that the overlap with the unpaired electron located primarily on the trigonal carbon is not disproportionately affected.

Molecular orbital calculations in the INDO approximation also support the perpendicular conformation **2b** for the 1-aziridylcarbinyl radical. Two approaches were taken with the calculations. First, a partial energy minimization of geometry was attained by utilizing the aziridine structure[9] and varying N–C_1, ϕ (angle between bisector of CNC angle and N–C_1 bond), C_1–H, HC_1H angle, and θ (angle between bisector of HC_1H and N–C_1 bond) in that order; ϕ and θ were then varied further to achieve an energy minimum (*cf.* **5**). An energy

5
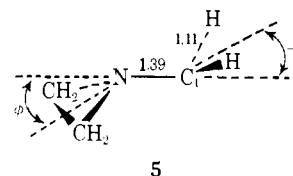
minimum was achieved for a nontwisted anti alignment with ϕ = 96° and θ = −36°. We believe that this geometry with the relatively large ϕ value is unrealistic and may be an artifact of the CNDO/INDO method.[10] This structure yields a^N = +2.72 G and $a_\alpha{}^H$ = +0.39

(9) L. E. Sutton, *Chem. Soc., Spec. Publ.*, No. 11, M 138 (1958).
(10) The CNDO/INDO semiempirical method neglects many two-electron integrals which represent electron repulsions and exchange interactions and this neglect gives too much weight to the forces remaining such as orbital overlap effects. In discriminating between two isomers, the structure displaying the greater number of bonds will oftentimes be incorrectly favored: E. I. Snyder, *J. Amer. Chem. Soc.*, **92**, 7529 (1970); R. Sustmann, J. E. Williams, M. J. S. Dewar, B. C. Allen, and P. v. R. Schleyer, *ibid.*, **91**, 5350 (1969); H. Iwamura, K. Morio, M. Oki, and T. L. Kunii, *Tetrahedron Lett.*, 4575 (1970). This idiosyncrasy of the CNDO/INDO method may be related to the unrealistic (?) value of ϕ for the partially energy-minimized geometry. It must be borne in mind, also, that a complete energy minimization could yield a considerably different geometry.

Danen, West / Esr Investigation of 1-Aziridylcarbinyl Radical
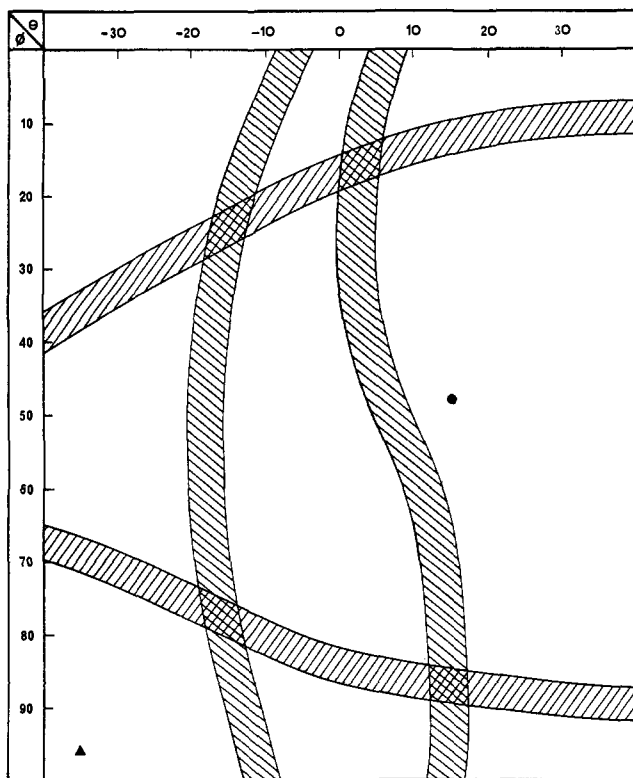
Figure 2. Nomograph in θ and ϕ (cf. 5) showing regions of acceptability of a^N and a_α^H for the 1-aziridylcarbinyl radical (2) calculated by INDO method assuming r_{C-N} = 1.38 Å: (▨) a^N; (▨) a_α^H; (▲) "minimum energy" anti geometry; (●) "minimum energy" syn geometry.

Figure 3. Nomograph in θ and ϕ (cf. 5) showing regions of acceptability of a^N and a_α^H for the 1-aziridylcarbinyl radical (2) calculated by INDO method assuming r_{C-N} = 1.47 Å: (▨) a^N; (▨) a_α^H; (■) minimum energy geometry calculated by INDO and STO-3G methods for H_2NCH_2.[6]

G which are at great variance with the experimental values for **2**. A nomograph in θ and ϕ utilizing the energy-minimized C_1-N and C_1-H bond lengths and HC_1H angle, 1.38 Å, 1.11 Å, and 118°, respectively, is shown in Figure 2. Four geometries are consistent with the observed hyperfine couplings (areas of intersection of the a^N and a_α^H lines) but none of these are similar to the "energy-minimized" geometry. Moreover, the "energy-minimized" structure for **5** is not similar to that obtained by both INDO and *ab initio* methods for the parent aminoethyl radical, H_2NCH_2 (ϕ = 45°, θ = −30°).[6] It may be noted that the "energy-minimized" structure for an assumed syn configuration of **5**, ϕ = 48°, θ = 15°, is very similar to that obtained for syn H_2NCH_2 (ϕ = 45°, θ = 20°).[6]

A second approach to the INDO calculations was to ignore the energy-minimized C–N distance of 1.38 Å and assign this distance a value of 1.47 Å as did Wood and Lloyd[6] in preparing a nomograph in θ and ϕ for H_2NCH_2. A nomograph constructed for a^N and a_α^H for the 1-aziridylcarbinyl radical is shown in Figure 3. It is noted that there are three regions of acceptability of the hyperfine coupling constants, a broad zone for an anti configuration with approximate values of ϕ = 50° and θ = −20° and two for syn geometries. By comparison of Figures 2 and 3 it is seen that the INDO calculated a^N values are quite dependent on the C–N bond length and other structural variables and one must be cautious in accepting any geometry for the 1-aziridylcarbinyl radical based on these calculations. Nonetheless, the similarity between the nontwisted anti configuration for **2** with ϕ = 50° and θ = −20°

predicted by INDO with the realistic[11] C–N value of 1.47 Å and the INDO and *ab initio* geometry predicted for H_2NCH_2 (ϕ = 45°, θ = −36°) allows us to favor this structure for **2**.

The value a_α^H = 17.07 G observed for **2** is considerably larger than that observed for $(CH_3)_2NCH_2$ (13.35 G)[6] reflecting more unpaired electron density on the trigonal carbon and/or less deviation from planarity for this carbon in **2**. Presumably this results from a somewhat diminished importance for contributing structure **6**

6
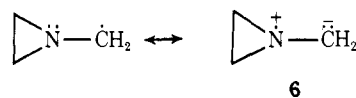
because of the enhanced s character of the nitrogen lone pair in this strained ring species. INDO calculations assuming ϕ = 50° and θ = 0° (*i.e.*, planar trigonal carbon) for **2** yield a π spin density of 0.854 and a charge of −0.0026 for the trigonal carbon and a^N = 15.98 G. An analogous calculation for H_2NCH_2 gives a slightly diminished spin density of 0.847 on carbon, an enhanced charge of −0.0179, and a^N = 12.19 G. As was pointed out above, the observed a^N of 10.68 G for **2** is larger than a^N for $(CH_3)_2NCH_2$ (7.03 G) in spite of the diminished relative importance of structure **6** because of the enhanced s character of the nitrogen lone pair.

From Figure 3 it may be noted that the trigonal carbon is calculated to be nonplanar with θ about −20° which may be accounted for on the basis of an electronegativity effect of the attached aziridine ring[12] or by back donation of electrons from the nitrogen (cf.

(11) L. E. Sutton, *Chem. Soc., Spec. Publ.*, No. 18, S19s (1965).
(12) L. Pauling, *J. Chem. Phys.*, **51**, 2767 (1969).

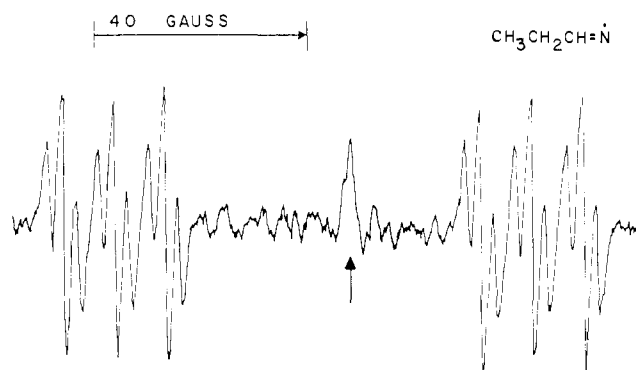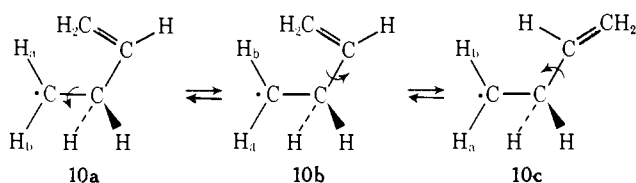**6).** Only 0.62 kcal/mol is required, however, to achieve a planar geometry about C_1.

A much larger amount of energy is necessary to twist the p orbital on C_1 out of alignment with the lone pair on nitrogen. The perpendicular conformation **2b** was calculated to be 4.19 kcal/mol more stable than the bisected alignment **2a**. These calculations assumed a planar geometry about the trigonal carbon and no attempt was made to optimize the geometry for either conformer. When compared to the calculated energy difference between the perpendicular and bisected conformation of the cyclopropylcarbinyl radical of 5.41 kcal mol^{-1} (bisected more stable),[4] a calculated nitrogen lone pair stabilization energy of about 9.6 kcal mol^{-1} is obtained.[13] However, it is important to realize that such INDO calculations probably overestimate the true energy differences by a factor of 2–4.[4,13] Nonetheless, the INDO calculations support the previous conclusion that the perpendicular conformation is preferred over the bisected conformation because of stabilization derived from resonance interaction of the unpaired electron and the nitrogen lone pair.

To gain further insight into the conformation of aziridylcarbinyl radicals and, in particular, to determine the amount of spin density at the trigonal carbon,[14] we attempted to generate the (1-aziridyl)-1-ethyl radical **7** from N-ethylaziridine (eq 3). However,

$$\triangleright\!\!N\!-\!CH_2CH_3 \xrightarrow[h\nu]{t\text{-}Bu_2O_2} \triangleright\!\!N\!-\!\dot{C}HCH_3 \longrightarrow$$

7

$$\dot{C}H_2CH_2N\!=\!CHCH_3 \quad (3)$$

8

even at temperatures as low as $-160°$, only the spectrum of the ring-opened radical **8** could be observed (Figure 4 and Table I); no spectrum attributable to **7** was produced.[15] Radical **8** is presumably formed from **7** in a manner analogous to the formation of **4** from **2** (eq 1). The apparent lowered stability of **7** as compared to **2** parallels the behavior of other aliphatic aminoalkyl radicals in which sequential substitution of the trigonal carbon with alkyl groups caused a decrease in stability of the radical.[6] A similar effect was not noted for a series of alkyl-substituted cyclopropylcarbinyl radicals.[3b]

The ring-opened radicals **4** and **8** presented an interesting comparison to the allylcarbinyl radical.[3a] The β-hydrogen hfsc's of radicals **4** and **8** (ca. 34 G) were somewhat larger than in the corresponding allylcarbinyl radical (28.53 G). Assuming the α-carbon spin density was identical with the ethyl radical and using the β-hydrogen hfsc of the ethyl radical as the freely rotating model, a conformational analysis was carried out employing the method of Heller and McConnell.[16] It

(13) P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, **75**, 3438 (1971). These authors conclude that the barrier to rotation in the cyclopropylcarbinyl radical cannot be more than 2–3 kcal/mol.

(14) H. Fischer, *Z. Naturforsch. A*, **20**, 428 (1965).

(15) The spectrum attributed to **8** could conceivably be due to the (1-aziridyl)-2-ethyl radical

$$\triangleright\!\!N\!-\!CH_2\!-\!\dot{C}H_2$$

We prefer the assignment to **8**, however, because of the close analogy of the rearrangement of eq 3 to that of eq 1. Moreover, in the absence of some stabilizing influence, radicals derived from primary C–H abstraction generally are not observed by esr under these conditions.

(16) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

Figure 4. Electron spin resonance spectra of **8** obtained by photolysis of N-ethylaziridine and di-*tert*-butyl peroxide in cyclopropane solution. Spectrum A was obtained at $-110°$; spectrum B was recorded at $-140°$ and shows clearly the diminished resolution of the third, fifth, and seventh peaks. These broadened peaks, corresponding to the $M_I = 0$ lines of the β protons, are illustrated with somewhat heavier marks of reduced height in the stick diagram.

was found that the average dihedral angle, γ, between the β C–H bond and the spin bearing p orbital is *ca.* 36°. This conformation is the same, as deduced for the allylcarbinyl, n-propyl, and n-butyl radicals from the temperature dependences of $a_\beta{}^H$.[17] However, examination of the spectra of **4** or **8** reveals that the peaks corresponding to the $M_I = 0$ line of the β protons are selectively broadened (*cf.* Figure 4). This is an example of an out-of-phase alternating line-width effect[18] in which a conformational rotation exchanges the β protons between different magnetic environments. Rotation about the C_β–C_γ bond with a frequency *ca.* 10^{-7}–10^{-8} sec^{-1} as depicted in **9** is consistent with this exchange

9

(**4**, R = H; **8**, R = CH$_3$)

process since this results in the two β protons, H_a and H_b, being exchanged between two different environments. The observation that the triplet due to the two α protons remains sharp over the temperature range investigated indicates that rotation about the C_α–C_β bond at least in **8**[19] is rapid on the esr time scale at these temperatures.

The behavior for **4** and **8** contrasts that observed for

(17) K. S. Chen, D. J. Edge, and J. K. Kochi, *J. Amer. Chem. Soc.*, **95**, 7036 (1973), and references cited therein.

(18) P. D. Sullivan and J. R. Bolton, *Advan. Magn. Resonance*, **4**, 39 (1970).

(19) The relatively poor signal to noise ratio in the spectrum for **4** precluded a detailed line-shape analysis.

Figure 5. Electron spin resonance spectrum of the imino radical 12 in an adamantane matrix at room temperature formed by X-ray irradiation of cyclopropylamine. The arrow marks a quartz impurity.

the allycarbinyl radical (10) in which an out-of-phase line-width effect in the α-proton splittings and an in-phase (4 and 8 exhibit out-of-phase effects) line-width effect in the β-proton splittings was observed. A significant difference exists, then, between the preferred conformation of the nitrogen-containing radicals 4 and 8 of the present study and 10. In the latter the double bond remains coplanar with C_α and C_β possibly as a result of homoconjugation between the double bond and the p orbital on the α carbon.[20] In 4 and 8, however, a coplanar alignment is not observed suggesting that a 1,3 interaction between the unpaired electron on C_α and the lone pair electrons on the nitrogen atom may be preferred over interaction with the double bond. Stabilization of a radical by an adjacent lone pair (1,2 interaction) is, of course, well documented. An additional electronic effect may be operative to destabilize the coplanar conformation of 4 and 8. By assuming conformation 9 the nitrogen lone pair is *not* aligned to interact with the C_α–C_β bond. We have shown by INDO calculations in previous studies[4] that C–C hyperconjugation is unfavorable for carbanions. It is plausible to assume that a similar destabilization is averted by the lone pair electrons on nitrogen in conformation 9.

The absence of an out-of-phase line-width effect in the α-proton splitting for 4 and 8 even at $-140°$ is notable. The higher barrier to rotation about the C_α–C_β bond in the allylcarbinyl radical[17] may result at least in part from a steric interaction between the α hydrogens and the γ and δ hydrogens as a result of the favored planar conformations of this radical (*cf.* 10a–c). Such steric interactions are minimized for 4 and 8 in conformation 9.

The presence of a small doublet hyperfine coupling due to a lone δ proton in 4 and the absence of such an interaction in 8 is noteworthy. It has been suggested that in the allycarbinyl radical the small doublet interaction is due to the trans δ hydrogen and, moreover, that the uniqueness of the δ protons supports a planar

(20) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 93, 846 (1971).

structure for allycarbinyl radicals. Yet in 4 a small coupling to one of the δ protons is observed even though this radical probably exists in a nonplanar geometry on basis of the line-width effects. It was thought that INDO calculations might demonstrate that one of the δ protons of 4 is more favorably oriented for interaction with the unpaired electron even in a nonplanar alignment. In fact, the calculations, assuming standard bond lengths and angles,[21] do not differentiate appreciably between the δ protons in either a nonplanar 4a or planar 4b conformation. Interestingly, the trans H in

4a   4b
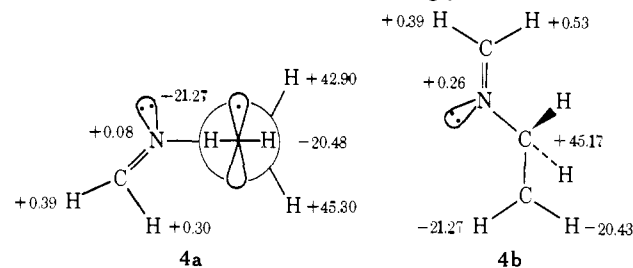
4b has a *smaller* calculated hyperfine coupling than the cis H.

The absence of a small doublet in the spectrum of 8 implies that this radical probably exists largely in a (presumably) trans geometry as depicted in 9 (R–CH₃). Substituted allylcarbinyl radicals normally exist as a mixture of cis and trans isomers, the relative amounts of which are determined by the cyclopropylmethyl radical precursors.[22]

(b) Cyclopropylamino Radical. It was thought that the cyclopropylamino radical could be generated by N–H abstraction from cyclopropylamine with photolytically produced *tert*-butoxyl radicals by analogy to the generation of the cyclopropylcarbinyl,[3] aziridino, and azetidino radicals.[5a] Alternatively, the *N-tert*-butoxyl-*N*-cyclopropylamino radical might be produced in analogy to the formation of *N*-alkoxy-*N*-arylamino radicals by the photolysis of solutions of anilines and di-*tert*-butyl peroxide.[1a] However, irradiation of samples which were 10% by volume cyclopropylamine and 10% di-*tert*-butyl peroxide in cyclopropane from -120 to $-60°$ produced only an esr spectrum consistent with the ring-opened radical 11 (eq 4). The hfsc's, $a_\alpha{}^H = 22.35$ G (2 H, 1:2:1 triplet)

$$\text{11, R = H or } (CH_3)_3CO$$
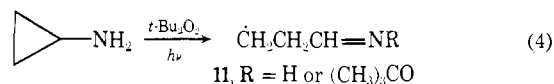
and $a_\beta{}^H = 28.80$ G (2 H, 1:2:1 triplet), were nearly identical with the allylcarbinyl radical 10 ($a_\alpha{}^H = 22.17$ G and $a_\beta{}^H = 28.53$ G) reported by Kochi, Krusic, and Eaton.[3a] There was no esr evidence for the cyclopropylamino radical or the 2-azetidyl radical. At temperatures lower than $-120°$ a broadened singlet was observed probably due to the fact that sample had frozen.

In another attempt to generate the cyclopropylamino radical, the adamantane technique of Wood and Lloyd was employed.[6] After X-ray irradiation at $-196°$ for 2 hr the esr spectrum consisted of a broadened line at temperatures between -140 to $0°$. The broadened line was replaced upon further warming by the spectrum shown in Figure 5. The hyperfine splitting constants

(21) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, p 111.
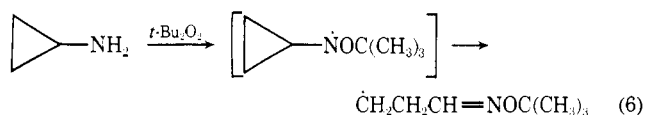(22) J. K. Kochi and P. J. Krusic, *Chem. Soc., Spec. Publ.*, No. 24, 147 (1970).

derived from this spectrum were $a^H = 2.80$ G (2 H, 1:2:1 triplet), $a^N = 9.40$ G (1:1:1 triplet), and $a^H = 79.5$ G (1 H, 1:1 doublet). The g value after correction for second-order effects is 2.0030. These spectral parameters are typical of imino radicals, RCH=N.[23] Even though the coupling of 79.50 G might be rationalized for the cyclopropylamino radical in the perpendicular conformation there was no evidence of an N–H coupling. Moreover, the g value of 2.0030 also is not consistent with amino radicals which have g values of ca. 2.0044.[5e]

Unfortunately, the experimental conditions employed were not successful in generating the cyclopropylamino radical. The results obtained, however, strongly suggest that the cyclopropylamino radical was formed but was followed by a facile ring opening. In adamantane, the ring opening was probably followed by an intramolecular hydrogen abstraction to form the imino radical.[12]

$$\triangleright\!\!-NH_2 \xrightarrow{\text{X-rays}} \dot{C}H_2CH_2CH=NH \longrightarrow CH_3CH_2CH=\dot{N} \quad (5)$$

12
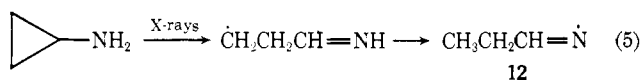
The fact that no imino radical was formed by photolysis of cyclopropylamine in the presence of di-tert-butyl peroxide may have been the result of the lower temperature of the system ($< -60°$ vs. $>0°$) or by the consideration that an alkoxyamino radical[1a] may have been formed prior to ring opening.

$$\triangleright\!\!-NH_2 \xrightarrow{t\text{-}Bu_2O_2} \left[\triangleright\!\!-\dot{N}OC(CH_3)_3\right] \longrightarrow$$
$$\dot{C}H_2CH_2CH=NOC(CH_3)_3 \quad (6)$$

INDO calculations suggest that the cyclopropylamino radical should prefer the bisected conformation **3a** with the nitrogen lone pair electrons eclipsing the cyclopropyl group.[24] This conformation is calculated to be more stable than either a perpendicular (**3b**) or bi-

ΔE, kcal/mol = 0.0   6.86   2.35
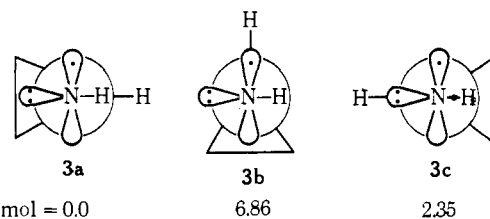
sected alignment with the hydrogen on nitrogen eclipsing the cyclopropyl group (**3c**) by 6.86 and 2.35 kcal/mol, respectively. The difference in energy between **3a** and **3b** is similar to the difference calculated for the bisected and perpendicular conformations of the cylopropylcarbinyl radical (7.21 kcal/mol, bisected more stable).[4] As noted above, however, such INDO calculations probably overestimate the true energy differences by a factor of 2–4.[4]

Experimental Section

The attempted generation of the cyclopropylamino radical in an adamantane matrix was accomplished by dissolving purified adamantane in freshly distilled cyclopropylamine and allowing the bulk of the amine to evaporate but trapping some in the adamantane matrix. The sample was then placed in a quartz tube and irradiated at $-196°$ for 2 hr with X-rays from a Norelco Type 12045B/3 X-ray diffraction unit (copper target, 45 kV, 20 mA) with the sample positioned about 2 in. from the target.

Chemicals. *N*-Methylaziridine. Following the method of Leighton, Perkins, and Renquist,[26] 2-methylaminoethylsulfuric acid was prepared from 2-methylaminoethanol and concentrated H_2SO_4.

Reaction of 2-methylaminoethylsulfuric acid with 40% aqueous NaOH, using the method of Wenker,[27] afforded *N*-methylaziridine in 36.5% yield; bp 24.5–26.0° (lit.[28] bp 23.2–23.8° (739 mm)).

N-Ethylaziridine. The preparation of *N*-ethylaziridine was achieved in the same manner as the synthesis of *N*-methylaziridine. Using 62.9 g (0.706 mol) of 2-ethylaminoethanol and 70.6 g of concentrated H_2SO_4, 94.6 g (0.56 mol) of 2-ethylaminoethylsulfuric acid was prepared. Reaction of 50 g (0.296 mol) of 2-ethylaminoethylsulfuric acid with 40% aqueous NaOH afforded *N*-ethylaziridine: bp 50.5–51.3° (lit.[29] bp 54.9–55.0°).

All other chemicals were commercially available.

(23) D. E. Wood, R. V. Lloyd, and D. W. Pratt, *J. Amer. Chem. Soc.*, **92**, 4115 (1970); P. Neta and R. N. Fessenden, *J. Phys. Chem.*, **74**, 3362 (1970).

(24) The calculations assumed the geometry of cyclopropane[25] with NH replacing one hydrogen with $r_{C-N} = 1.47$ Å and $\angle CNH = 120°$.

(25) O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964).

(26) P. A. Leighton, W. A. Perkins, and M. L. Renquist, *J. Amer. Chem. Soc.*, **69**, 1540 (1947).

(27) H. Wenker, *J. Amer. Chem. Soc.*, **57**, 2329 (1935).

(28) H. T. Hoffman, Jr., G. E. Evans, and G. Glockler, *J. Amer. Chem. Soc.*, **73**, 3028 (1951).

(29) F. J. Buist and H. J. Lucas, *J. Amer. Chem. Soc.*, **79**, 6157 (1957).